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Two new steroidal glucosides from *Ophiopogon japonicus* (L.f.) Ker-Gawl

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Abstract

Two new steroidal glucosides, 26-*O*-β-D-glucopyranosyl (25*S*)-furost-5-ene-1β,3β,22α,26-tetraol 1-O-β-D-xylopyranosyl-(1 → 3)-[α-L-rhamnopyranosyl-(1 → 2)]-β-D-fucopyranoside and (25R) spirost-5-ene-3β,14α-diol-3-β-*O*-β-L–rhamnopyranosyl-(1 → 2)-[β-D-xylopyranosyl(1 → 4)]-β-D-glucopyranoside, were isolated from the *Ophiopogon japonicus* (L.f.) Ker-Gaw. Their structures were elucidated by spectroscopic methods.

Keywords: *Ophiopogon japonicus* (L.f.) Ker-Gawl; Steroidal glucosides; Liliaceae

The tuber of *Ophiopogon japonicus* (L.f.) Ker-Gawl is a Chinese traditional medicine named ''maidong''. The tuber was recorded to have various medical functions for curing cardiovascular diseases and bacterial infections, especially heart diseases. Phytochemical studies on this plant were reported previously [1]. In the search for new and bioactive components from Chinese traditional medicine, we investigated the tubers of *O. japonicus*. In the present paper, we report the isolation and structure elucidation of two new steroidal glucosides by using 1D, 2D NMR techniques, ESI-MS analysis as well as chemical methods.

Compound **1**, amorphous powder, $[\alpha]_D^{20}$ −29.5 (c 0.15, MeOH). Its IR spectrum (KBr, ν) showed absorptions at 3612 (OH), 1625 (C=C) cm^{-1}. An acidic hydrolysis of **1** with mineral acid afforded glucose, rhamnose, fucose and xylose as the sugar components. Its HRESI-MS showed $[M-H]^-$ at *m/z* 1033.52183 (calcd. 1033.52195), corresponding to the formula $C_{50}H_{82}O_{22}$. Its ESI-MS showed significant ion peaks at *m/z* 887 (M-146-H)$^-$, 901 (M-132-H)$^-$, 755 (M-132-146-H)$^-$, and 609 (M-132-146-146-H)$^-$. Its ^{1}H NMR spectrum (Table 1) showed diagnostic signals of four methyl groups at δ 0.90 (s, 3H, CH_3-18), 1.39 (s, 3H, CH_3-19), 1.22 (d, 3H, J = 7.0 Hz, CH_3-21), 0.99 (d, 3H, J = 6.6 Hz, CH_3-27), and three oxymethines at δ 3.83 (m, ^{1}H, H-1), 3.68 (m, ^{1}H, H-3), 4.99 (m, ^{1}H, H-16), one oxymethylene at δ 3.47 (dd, ^{1}H, J = 7.0, 9.5 Hz, H-26), 4.06 (m, ^{1}H, H-26), and four anomeric protons at δ 4.65 (d, ^{1}H, J = 7.5Hz), 4.77 (d, 1H, J = 7.5Hz), 4.94 (d, ^{1}H, J = 7.5 Hz), 6.34 (s, ^{1}H). Its ^{13}C NMR spectrum showed signals of

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Table 1
^{13}C NMR and ^{1}H NMR data of sugars **1** and **2** in C_5D_5N

Compound **1**			Compound **2**		
No.	δ_C	δ_H (*J*, Hz)	No.	δ_C	δ_H (*J*, Hz)
3-O-Fuc-1	100.4	4.65 (d, 7.5)	3-O-Glc-1	100.1	4.82 (d, 7.7)
2	74.7	4.02	2	77.4	4.11
3	85.5	4.06	3	77.7	4.20
4	72.7	4.58	4	81.7	4.08
5	71.6	4.23	5	76.4	3.95
6	17.1	1.48 (d, 6.2)	6	61.8	4.50, 4.28
Rha-1	101.7	6.34 (s)	Rha-1	102.1	6.23 (br, s)
2	70.6	4.21	2	72.6	4.79
3	72.5	4.77	3	73.0	4.65
4	74.2	4.07	4	74.3	4.42
5	68.2	4.85	5	69.8	4.48
6	19.1	1.72 (d, 6.5)	6	18.8	1.46 (d, 5.6)
Xyl-1	106.6	4.94 (d, 7.5)	Xyl-1	105.9	4.99 (d, 7.0)
2	74.9	3.43	2	75.1	3.92
3	78.3	3.95	3	78.5	4.06
4	70.7	3.75	4	70.9	4.15
5	67.03	4.25, 3.68	5	67.0	4.12, 3.56
26-O-Glc-1	105.1	4.77 (d, 7.5)			
2	75.3	4.06			
3	78.5	4.21			
4	69.3	4.77			
5	78.4	3.99			
6	62.7	4.52, 4.33			

four angular methyl groups, four carbons bearing a hydroxyl group and four anomeric carbons. In a comparison of the ^{13}C NMR signals for aglycone of **1** (Table 2) with those of known saponin 26-*O*-β-D-glucopyranosyl-(25*S*)furost-5-ene-1β,3β,22α,26-tetraol-1-*O*-β-D-fucopyranoside (compound 113) [2], all signals due to the aglycone of **1** were almost superimposable with those of compound 113, indicating the aglycone of **1** was same as that of compound 113 and its 1- and 26-hydroxy groups carried a sugar moiety, respectively.

As described above, the sugar moiety of **1** consisted of glucose, rhamnose, fucose and xylose. The coupling constants of the anomeric protons revealed the β configurations for glucoses, fucose and xylose, and α configurations

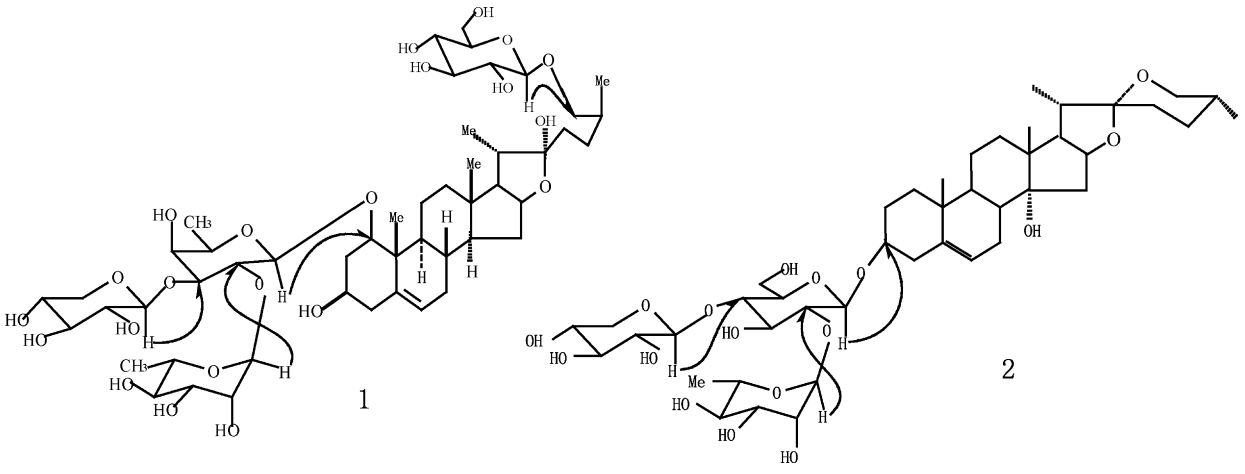

Fig. 1. The structure and HMBC of compounds **1** and **2**.